Studies on the Determination of Arsenic. II : Colorimetric Determination of Arsenic

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Synopsis

New colorimetric determination of arsenic was studied applying molybdenum blue using hydrazine sulphate as reducing agent. This method was tried as a routine analysis and also as a rapid analysis for arsenic in iron, steel and iron ore, and satisfactory results were obtained.

I. Introduction.

In the first paper, a method for the estimation of arsenic in iron, steel and iron ore by which arsenic is determined by iodometry after separating as sulphide, has been reported. However, that method is not suitable for small quantities of arsenic, therefore, a colorimetric method has been studied. Molybdenum blue method as the colorimetry for arsenic has been often reported. Namely arsenate ion like phosphate ion an acidic solution with ammonium molybdate and some reducing agent, forms a stable bluish complex which composition is $(MoO_2 4MoO_3)_2H_3AsO_4$, but arsenite ion does not form the compound. Stannous chloride[1] was used already as the redcuing agent for the purpose, now the use of hydrazine sulphate was tried as a new reducing agent and the conditions for the colorimetry were studied with the Pulfrich's photometer. At first, a suitable condition of the colorimetry was established by some fundamental experiment.

II. Fundamental experiments

Extinction coefficient E was estimated with the Pulfrich's photometer under various conditions. A brilliant lamp as the light source, red filter S 72 and 20 mm cells were used. One of the cells was filled with a sample solution and the others with blank solution and then E was estimated. When the change of yellow colour without arsenic was estimated, the other cell was filled with distilled water.

1. Concentration of acid.

Effect of concentration of hydrochloric acid, sulphuric acid, perchloric acid and nitric acid for the colouration of arsenic was studied. 0.20 mg of arsenic (sodium arsenate solution) was taken and various amount of acids, 7 ml of 1% ammonium molybdate solution and 10 ml of hydrazine sulphate solution were added and then its total volume was made up to 100 ml. This solution was heated for about 10 minutes in a boiling water bath then cooled with cold water and the extinction coefficient was estimated. The relation graph obtained is shown in Fig. 1 (E is the mean value of two estimations).

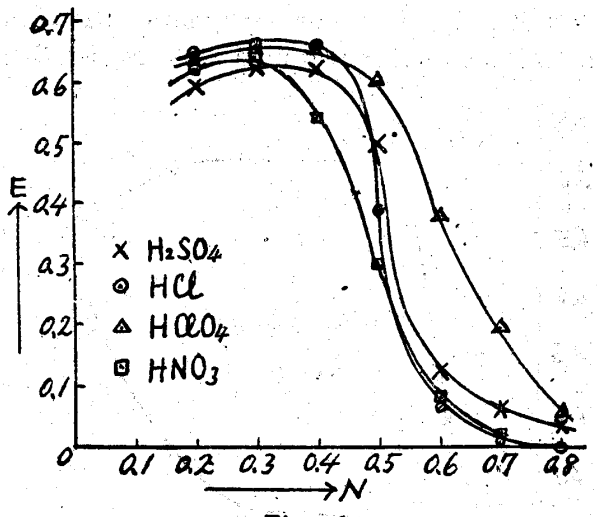

Fig. 1.

This shows that a constant colouration is given in a definite concentration of the acid, but this curve changed according to the

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amount of ammonium molybdate. For example, the result shown in Fig. 2 was obtained when 5 ml, 7 ml and 10 ml of 1% molybdate solution was used in a sulphuric acid solution. It has been shown by these results that a definite colouration occurs in the concentration of 0.3—0.4 N of sulphuric acid, hydrochloric acid or perchloric acid and of 0.3 N of nitric acid with 7 ml of ammonium molybdate solution, and also in the concentration of 0.3—0.5 N of sulphuric acid with 10 ml of ammonium molybdate.

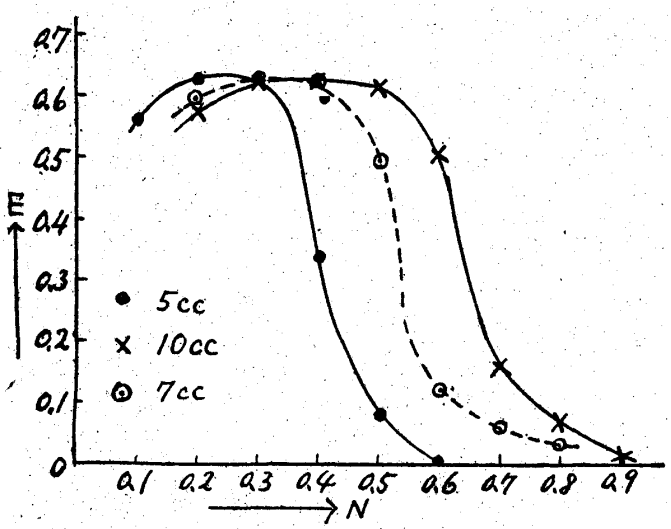

Fig. 2.

2. Amount of ammonium molybdate solution.

Experiments on the effect of ammonium molybdate for the colouration were made, using various amounts of it. 0.20 mg of arsenic was taken and various amounts of ammonium molybdate was added, and after an addition of 10ml of 1% hydrazine sulphate, the concentration of sulphuric acid was adjusted to 0.3 N in the solution, the volume of which was 100ml in the total, then it was treated as in the preceding experiment. The results obtained are shown in Fig. 3. These results show that 5–10ml of ammonium molybdate give a constant colour.

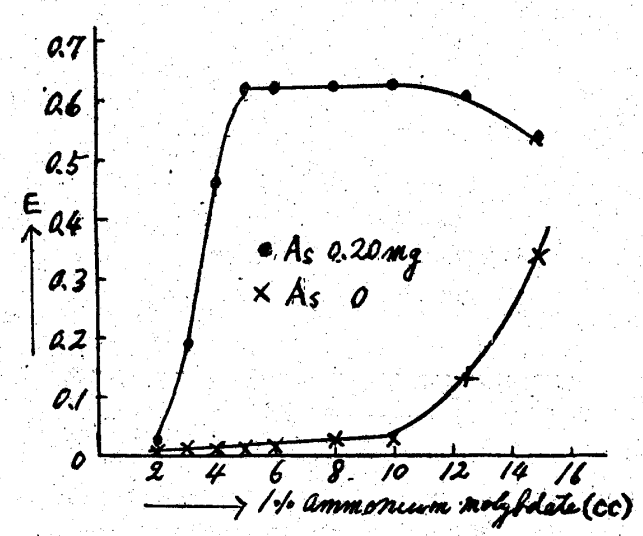

Fig. 3.

3. Amount of hydrazine sulphate.

The effect of the amount of hydrazine sulphate solution for use was studied. Under the same conditions as in the preceding experiment, excepting for the use of 5ml of ammonium molybdate solution, experiments were performed, using various amounts of 1% hydrazine sulphate solution. The results obtained show that the amount of hydrazine sulphate produces only a small effect as shown in Fig. 4

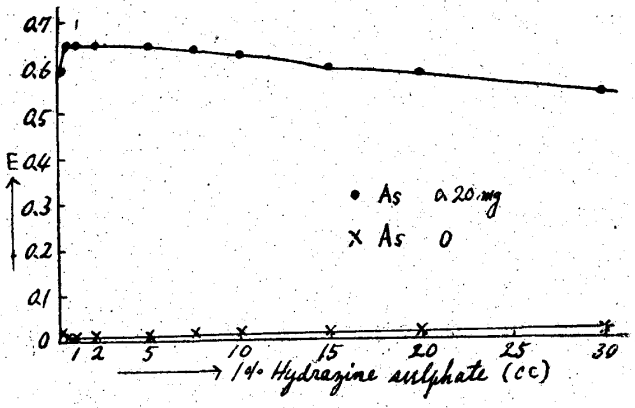

Fig. 4.

4. Time of heating.

The influence of time of heating for the colouration and the stability of the colour in hot solution were studied. 100 ml solution in the total, containing sulphuric acid at 0.3N, 0.10 mg of arsenic, 7 ml of 1% ammonium molybdate, 10 ml of 1% hydrazine sulphate, were heated in a boiling water bath for 5, 10, 20, 30 and 60 minutes respectively and E was measured. The results show that no effect was recognized for a time from 5 to 60 minutes, but heating for less than 5 minutes did not give perfect colouration.

5. Stability of colour generated.

E of the colour generated by heating for 10 minutes under the same conditions as in experiment 4, was measured after standing at room temperature for various time from 5 minutes to 20 hours, and this blue colour was so stable that no effect could be recognized. Moreover, the extinction coefficient E of a solution containing 0mg, 0.08mg or 0.16 mg of arsenic was measured at every 24

hours for 10 days and no change was recognized. The blue colour was stable, but a yellow colour of the blank solution changed slowly to faint.

6. Relation between the amount of arsenic and extinction coefficient.

The change of colouration against the amount of arsenic was measured.

(a) Extinction coefficient E of 0.3 N, 0.4 N or 0.5 N sulphuric acid solutions, containing various amounts of arsenic was measured respectively. The relation between E and the amount of arsenic are shown in Fig. 5.

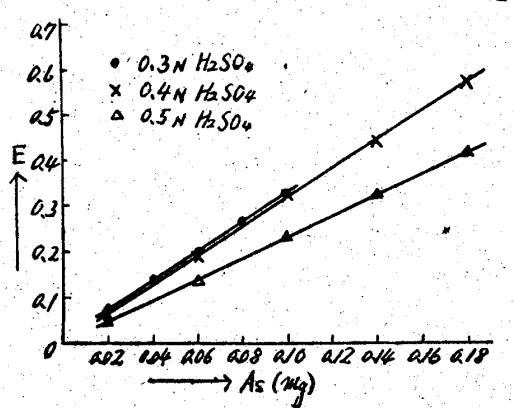

Fig. 5.

As shown in Fig. 5, all curves are linear and show that the colour is generated quantitatively. Two straight lines under 0.3N and 0.4 N acidity coincided, this fact shows that the same colouration is given in a range from 0.4N to 0.3N of the acid.

(b) Experiments under similar conditions as (a) were done with hydrochloric acid, perchloric acid, and nitric acid, and the same results were obtained.

In all cases, the straight line is obtained and the colouration is constant in a definite concentration of the acid.

7. Influence of other ions.

(a) Ammonium salts. The extinction coefficient of solutions which contained 10 g of ammonium sulphate and which colours were developed in 0.3 N sulphuric acid solution with 7ml of 1% ammonium molybdate solution and 10 ml of 1% hydrazine sulphate solution against various amounts of arsenic, was measured. They coincide in the absence of ammonium salt.

(b) Copper, cadmium, linc and manganese.

Experiments under the same conditions as above were tried with the addition of 20 mg of copper and no effect was recognized, but when larger amounts of copper was added, blue colour of copper ion itself interfered. Under the same condition, effects of 1g of cadmium or zinc or manganese were studied and all these metals give no effect.

(c) Iron. Adding 20mg of iron against various amounts of arsenic under the same condition, the extinction coefficient E was measured and arsenic was recognized to be determinable without any effect, but the colouration became slow according to the amount of iron. The time required for the colouration and the amount of iron contained are shown in Table 1.

Table 1.

$Fe^{\cdots}$ mg	Time required for colouration min
10	2—3
20	4—5
30	6—7
50	7—9

This is due to the fact that arsenic compound is reduced after ferric ion.

(d) Silicon. Silicon gives the same colouration as arsenic in acetic acid solution, but not in 0.3 — 0.4 N sulphuric acid solution. According to the results of the experiment, 2mg of silicon gives no effect, but very large amounts of silicon produces colouration.

(e) Phosphor. Phosphor is coloured the same as arsenic. The results obtained in 0.3N sulphuric acid solution has shown that phosphor gives the same colouration as that of arsenic when the amount of phosphor is converted into arsenic.

8. Analytical procedure.

The procedure for the colorimetric determination of arsenic by molybdenum blue method using hydrazine as the reducing agent was as follows.

Arsenate, containing 0.02—0.2 mg of arsenic, was taken and 10ml of 3N sulphuric acid or 3 N hydrochloric acid, 7ml of 1% ammonium molybdate solution and 10 ml of 1% hydrazine sulphate were added and its total volume was adjusted to 100ml with water. Then, it is heated in a boiling water bath for about ten minutes then cooled after perfect colouration, and the colorimetry was done with the Pulfrich's Photometer or some other colorimeters.

III. Colorimetric determination of arsenic in iron, steels and iron ore

The colorimetric determination of arsenic in iron, steels and iron ores was made by the method obtained by the preceding fundamental experiments.

(1) Analytical procedure.

(a) Iron and steels. Sample 0.1—1.0 g, according to its arsenic content, was taken and dissolved in 6N nitric acid by heating, then arsenic was separated from iron as metallic state by the method described in the 3rd or 4th papers of this series or as sulphide according to the preceding papers and the metallic arsenic or sulphide obtained was dissolved in nitric acid and oxidized with a few drops of potassium permanganate solution. The total or some part of the solution was taken and neutralized with sodium hydroxide using phenolphthalein as an indicator and then the colorimetrical determination was made by the method described below.

(b) Iron ore. Sample 0.1—1.0g was dissolved in aqua regia and sulphuric acid was added and then heated to white fume. The other procedure was followed as in(a). If a sample could not be dissolved perfectly in aqua regia, it must be fused with sodium peroxide and dissolved in water and then the procedure is continued as above.

(2) Colorimetry.

(a) Pulfrich's photometer. The amount of arsenic is estimated on the graph constructed by known amounts of arsenic and their extinction coefficient was estimated as in the fundemental experiment described above.

(b) Duboscq's or Kober's colorimeter.

When these are used, a standard solution of arsenic which contains known amounts of it is prepared, then some part of it is taken according to the amount of arsenic expected in the sample and the colour develops simultaneously with the sample.

(c) Ukena's colorimeter. Molybdenum blue with arsenic and hydrazine sulphate is so stable that a series of the coloured solution contained arsenic from 0.0 mg to 0.2 mg by 0.02 mg has been prepared in tubes of the colorimeter and compared with the sample solution to estimate the amount of arsenic. This method is convenient for a routine analysis of arsenic. This coloured standard can be used for a week, but a pale yellow tint of the solution which contains smaller quantities of arsenic tends to change slowly.

(3) Experimental results.

The results estimated with the Pulfrich's photometer by the procedure for some of iron, steel and limonite are shown in Table 2.

Table 2.

Sample	Sample taken g	Method of dissolution	Extinction coefficient E	As obtained mg	As (mean) %	Error %
Pig iron (As: 1.195%)	0.0100	Dissolved in 6N HNO_3	0.431 0.434 0.432	0.119 0.120 0.119	1.193	−0.002
Pig iron (As: 0.59%)	0.0100	Dissolved in 6N HNO_3	0.219 0.218 0.219	0.0595 0.0595 0.0595	0.595	+0.005
Carbon steel (As: 0.33%)	0.0200	Dissolved in 6N HNO_3	0.241 0.242 0.242	0.066 0.066 0.066	0.330	0.000
Iron ore (As: 0.902%)	0.0100	Dissolved in HNO_3+HCl	0.331 0.382 0.331	0.090 0.091 0.090	0.903	+0.001
Iron ore (As: 0.902%)	0.0100	Fused with Na_2O_2	0.331 0.331 0.332	0.090 0.090 0.091	0.903	+0.001
Limonite (As: 0.070%)	0.1000	Fused with Na_2O_2	0.256 0.256 0.256	0.070 0.070 0.070	0.070	0.000

IV. Rapid analysis of arsenic in iron, steels and iron ore

As is clear from the fundamental experiment, the determination is possible even in the presence of nitric acid, iron less than 50 mg and silicon less than 10 mg. Hence, arsenic in iron and steel which contain larger quantities is determinable without any separation. But in this method, phosphorus is so coloured at the same time as mentioned already that a sum of arsenic and phosphorus is obtained, hence, phosphorus must be determined by another method and be deducted from the total amount. The coloration of phosphorus is 2.416 times that of arsenic, therefore the sample must be taken with consideration of this fact.

(1) Procedure.

0.1 g of the sample is taken, dissolved in 10—30ml of 6 N nitric acid and heated to boiling, then oxidized with few drops of potassium permanganate solution, transfered into a measuring flask of 250 ml, diluted to the mark with water, the 25 ml of it is taken and neutralized with sodium hydroxide. 10 ml of 3 N sulphuric acid, 7 ml of 1% ammonium molybdate and 10 ml of 1% hydrazine sulphate are added to it and made up to 100 ml with water, then heated in a boiling water bath, cooled after colouration and the colorimetry was carried out.

Table 3.

Sample	Sample taken g	Extinction coefficient E	As+P (P is calculated as As) mg	P (culculated as As) mg	As mg	As (mean) %	Error %
Pig Iron As: 1.195% P : 0.217%	0.0100	0.608 0.607 0.608	0.172 0 171 0.172	0.0524	0.1196	1.196	+0.001
Pig Iron As: 0.59% P : 0.246%	0.0100	0.427 0.427 0.426	0.119 0.119 0.118	0.0591	0 0591	0.591	+0.001
Carbon steel As: 0.33% P : 0.0095%	0.0200	0.260 0.261 0.271	0.0705 0.0705 0.0705	0.0046	0.0659	0.330	0.000
Iron Ore As: 0.902% P : 0.109%	0.0100	0.421 0.421 0.420	0.117 0.117 0.116	0 0263	0.0903	0.903	+0.001
Limonite As: 0.070% P : 0.669%	0.0100	0.614 0.615 0.614	0.169 0 170 0.169	0.162	0.0073	0.073	+0.003

(2) Experimental results

Some of iron, steel and limonite is anaylzed by the preceding procedure and the results obtained are shown in Table 3. These results were obtainnd by means of Pulfrich's photometer. All results by the rapid method are compared with them by the standard method.

(3) Time required for the rapid enalysis.

The time required for the preceding analysis is shown in Table 4. The time for the colouration varies according to the amount of iron present.

Table 4.

Procedure	Time (min)		
	Steel	Pig iron	Limonite
Sample taken	1	1	1
Dissolution	1—2	1—3	2—3
Filtration	—	2—3	3—5
Boiling and oxidation with $KMnO_4$	1	1	1
Dividing solution	1—2	1—2	1—2
Neutralization and addition of reagent	1	1	1
Colouration	2—9	2—9	2—9
Cooling	1—2	1—2	1—2
Colorimetry	1	1	1
Calculation	1	1	1
Total	10—20	12—24	14—26

In conclusion the author wishes to express her heartfelt thanks to Prof. H. Gotô for his valuable suggestions during the work.

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